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Mixed ligand complexes of Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) with Methionine and 8-Hydroxyquinoline

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The stability constants of mixed Cu (II), Ni (II), Co (II), Zn (II) and Cd (II) complexes containing methionine as a primary ligand and 8-hydroxquinoline as a secondary ligand have been determined in aqueous medium at an ionic strength 0.2M $NaC10_4$ at 30, 40 and 50 ($\pm$1°c).The studies revealed the formation of mixed ligand complexes containing 1:1:1 molar ratio of metal and two ligands. The modified method of Irving and Rossotti was used for the potentiometric titrations. The trend of the stability constants of the mixed ligand complexes of the metal ions is found to be.

Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II)

This trend of metal ions is further confirmed by the values of free energies. The values of stability constants decrease with increase of temperature.

The thermodynamic parameters-changes in free energy (ΔF°), enthalpy (ΔH°) and entropy (ΔS°) have also been calculated.

Literature survey[1-3] reveals that not much work has been done on mixed ligand complexes containing methionine.Therefore; it was preferred to use methionine as a ligand. In the present studies the stability constants (log K^{MA}_{MAB}) of the mixed ligand complexes of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} with methionine using as a primary ligand and 8-hydroxyquinoline as a secondary ligand have been determined by applying the modified method of Irving and Rossotti,[4-5].

The two ligands A and B having similar coordinating tendencies, combine simultaneously with the metal ion. If the reaction M+A$\rightleftharpoons$MA takes place at lower pH and

MA specy is stable at higher pH, then the formation of mixed ligand complex MAB can be determined by using the Irving and Rossotti method.

The thermodynamic parameters free energy (ΔF°), enthalpy (ΔH°) and entropy (ΔS°) have been calculated by using the temperature coefficient and GibbsHelmholtz equations.

MATERIAL AND METHOD

Methionine (E. Merck), $HC10_4$ (E.Merck), $NaC10_4$ (Reidel) and other chemicals of Analar BDH grade were used. The solutions of metal per chlorates were prepared by dissolving the metal carbonates in perchloric acid till no further salt was soluble. Then the solutions were filtered through G_4 sintered crucible and the metal ions were estimated by standard methods.[6]

The solution of methionine was prepared by dissolving it in conductivity water. The Hydroxyquinoline hydrochloride solution was prepared by dissolving 8-hydroxyquinoline in calculated quantity of HCl acid.

The pH titrations was carried out with a Philips digital pH meter (pp9045) with an accuracy pH range $\pm$ 0.02 unit at 30,40 and 50 ($\pm$1°c) maintaining the temperature constant with the help of a thermostat. The solutions were mixed in 1:1:1 ratio and the volume of each solution to be titrated was kept 50 ml and its ionic strength (μ) was maintained at 0.2M with $NaC10_4$solution.

The following mixtures of solutions were titrated against 0.2M NaOH solution and were repeated for the accuracy.

1. $2x10^{-2}$M $HC10_4$
2. $2x10^{-2}$M $HC10_4$+ $2x10^{-3}$M HQ HCI
3. $2x10^{-2}$M $HC10_4$+ $2x10^{-3}$M metal perchlorate + $2x10^{-3}$M methionine.
4. $2x10^{-2}$M $HC10_4$+ $2x10^{-3}$M metal perchlorate + $2x10^{-3}$M methionine + $2x10^{-3}$M HQ HCl.

After mixing the solutions, they were allowed to equilibrate by keeping them for one hour and each of the mixture was titrated against 0.2M NaOH solution at different temperatures.

The ml of alkali added was plotted against pH observed. The following four titration curves obtained are referred as:

A. Acid titration curve.

B. Secondary ligand titration curve.

C. Primary complex titration curve.

D. Mixed ligand complex titration curve.

From the nature above curves, the values of $\bar{n}$ were calculated by the modified Irving Rossotti method[4,5].

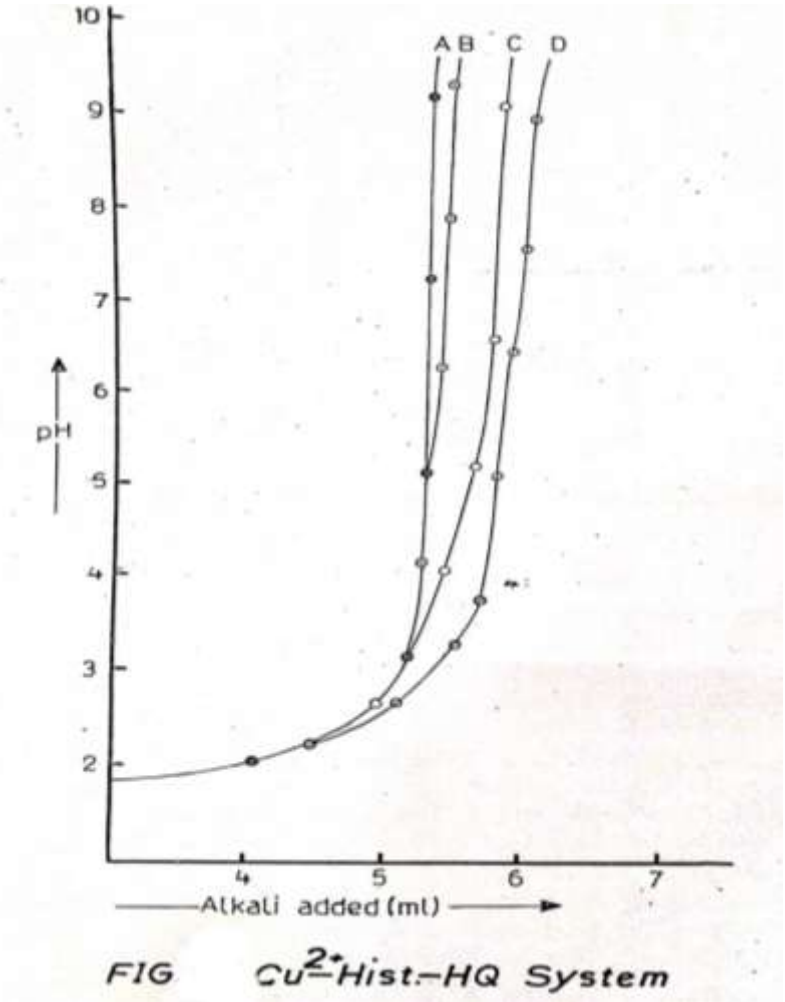

FIG Cu^{2+}-Hist-HQ System

RESULT AND DISCUSSION

The pK values of 8-hydroxyquinoline were calculated by Chabrek and Martell method[7] and are in agreement with the literature vlaues[8]. The value of $\bar{n}$(the average number of secondary ligand molecules attached with the primary complex) was calculated as discussed earlier[3].

For example, the titration curves at 30°c for the system Ni (II)-Methionine-HQ are shown in the fig. I, the nature of the curves indicates that the primary complex is formed at very low pH. The curve (D) for mixed ligand complex overlaps the primary complex curve (C) up to pH 3.70. This indicates that the secondary ligand (HQ) does not combine with primary complex in this pH range. The separation of theses curves begins at pH 3.70 i.e. due to self dissociation of secondary ligand.

At pH 4.30 the secondary ligand combines with the metal primary ligand complex. The light greenish yellow colour of the solution darkens at pH 3.70. which also supports the formation of mixed ligand complex.

The difference between the curve (A) and curve (B) is subtracted from the difference of curves (C) and (D) at various values of pH for calculating the $\bar{n}$values. The values of log K^{MA}_{MAB} are evaluated at $\bar{n}$ = 0.5 from the curve of $\bar{n}$vs pL and are summarized in Table 1. The error limits are 0.06 log units.

Similar curves are obtained for other system also and the results are given in the Table 1.

Table 1:- Stability constants of Mixed ligand complexes at different temperatures.

S.No.	System	Log K^{MA}_{MAB}		
		30°c	**40°c**	**50°c**
1.	Cu(II)-Methinonine - HQ	9.79	9.52	9.37
2.	Ni(II)-Methinonine – HQ	8.50	8.38	8.22
3.	Co(II)-Methinonine – HQ	8.44	8.27	8.12
4.	Zn(II)-Methinonine – HQ	8.39	8.17	8.03
5.	Cd(II)-Methinonine – HQ	8.19	8.07	7.88

THERMODYNAMIC PARAMETERS

The values of the changes in free energy (ΔF°) enthalpy (ΔH°) and entropy (ΔS°) have been calculated at three different temperature and at constant ionic strength of 0.2M $NaC10_4$ with the help of standard equations. The values are summarized in Table 2.

Table 2:- Thermodynamic Parameters of mixed ligand complexes

($\mu = 0.2M$ $NaC10_4$)

S. No.	System	Tem ^oc	$-\Delta F°$ (K cal mol^{-1})	$-\Delta H°$ (K cal mol^{-1})	$\Delta S°$ (cal mol^{-1} deg^{-1})
1.	Cu^{II}-Methionine-HQ	30 40 50	13.57 13.63 13.84	9.40	13.51
2.	Ni^{II}- Methionine - HQ	30 40 50	11.78 12.00 12.14	6.26	18.33
3.	Co^{II}- Methionine - HQ	30 40 50	11.70 11.84 12.00	7.16	14.95
4.	Zn^{II}- Methionine - HQ	30 40 50	11.63 11.70 11.86	8.06	11.62
5.	Cd^{II}- Methionine - HQ	30 40 50	11.35 11.55 11.65	6.94	14.72

Discussion

The stability constant of different complexes investigated here follow the order.

$$Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+}$$

Which agrees well with the Irving-Williams order[9,10]. This trend of metal ions is further confirmed by the values of free energies (Table 2). The values of stability constants decrease with the increase in temperature indicating that low temperature is favourable for complex formation.

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